In situ experimentally determined dissolution rates of biogenic calcites along a North Pacific transect between Hawaii and Alaska (KM1712 expedition) in August 2017

Website: https://www.bco-dmo.org/dataset/856409
Data Type: Cruise Results
Version: 2
Version Date: 2022-08-03

Project
» Ocean Acidification - Collaborative Research: Measuring the kinetics of CaCO3 dissolution in seawater using novel isotope labeling, laboratory experiments, and in situ experiments (CaCO3 dissolution)

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Abstract
This dataset includes biogenic and inorganic calcite and aragonite dissolution rates from the CDisK-IV cruise in the North Pacific Ocean, August 2017. We include niskin incubator alkalinity, pH, silicate, phosphate, and nitrate data, as well as calculated saturation state and dissolution rates. Rates are reported in units of g/g/day and also g/cm2/day, normalized by the specific surface areas of the materials used. Dissolution rates of inorganic aragonite and calcite, along with biogenic E. huxleyi liths, a planktic foraminifera assemblage, and a benthic foraminifera Amphistegina species, are provided, for 4 out of the 6 stations occupied on the cruise.

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Coverage

Spatial Extent: **N**:49.683 **E**:-148.3 **S**:27.75 **W**:-155.283
Temporal Extent: 2017-08-06 - 2017-08-26

Methods & Sampling

The methodology for measuring dissolution rate follows published methods in Naviaux et al., 2019 and Dong et al., 2019. The ratio of the dissolving solid was measured following methods of Subhas et al., 2018.

Dissolution experiments were conducted *in situ* using modified Niskin incubators, described in detail by Naviaux et al. (2019) and Dong et al. (2019). In this study, we dissolved bleached, ^{13}C-labeled *E. huxleyi* liths. A total of 20 coccolith dissolution experiments were conducted at depths between 240 to 1000 meters at Stations 2 to 5 with temperatures ranging from 2.4 to 4.8 degrees Celsius and Ωcalcite from 0.96 to 0.67. We conducted one experiment with a planktic foraminiferal assemblage, cultured and ^{13}C -labeled as described in Subhas et al. (2018). Briefly, roughly 0.5 to 1.5 milligrams (mg) of labeled biogenic calcite was sealed in between 47mm "Nuclepore" polycarbonate membrane filters (0.8 um pore size). These packets were then mounted inside the Niskin incubators. The incubators were hung on a hydrowire, sent down to depth, and triggered closed. The Niskin reactors remained closed at depth for 24 to 58 hours and were sampled for silica, SRP, nitrate, alkalinity, pH, and $\delta^{13}C$ -DIC upon recovery. Niskin data were quality checked by comparing SRP, silica, and nitrate to ambient water-column values obtained via CTD/rosette deployments on the same cruise. Saturation states in the Niskin reactors were determined from Alk-pH pairs, input into CO2SYS along with the temperature, salinity, depth, SRP, and silica concentrations at which the reactor was deployed. Dissolution rates were calculated by taking the difference between the final incubator and ambient water column $^{13}C/^{12}C$ ratios, multiplied by the [DIC] and the mass of seawater (1.126 kg) inside the incubators, and divided by the incubation time. Rates calculated in this way are in units of g $Ca^{13}CO_3$ g $CaCO_3^{-1}d^{-1}$. Biogenic materials were not 100% labeled and rates were scaled for the extent of isotope labeling following Subhas et al. (2018). Briefly, when the amount of ^{13}C in the dissolving material is substantially enriched above natural abundance ($^{13}C/^{12}C$~0.01), isotope ratio differences can be multiplied by a correction factor of $(Rs+1)/Rs$, where Rs is the $^{13}C/^{12}C$ ratio of the dissolving solid (i.e. a reduced form of Eq. 3 from Subhas et al. (2018) when $Rs >> R_1, R_2$). One batch of *E. huxleyi* was used for the majority of the dissolution rates shown here (Rs = 0.928). One experiment using the original batch of bleached *E. huxleyi* (Rs = 20, Subhas et al. 2018) was also run. The planktic foraminifera assemblage from Subhas et al. (2018) was used (Rs = 1.6). Dissolution rates were normalized further by the specific surface areas of *E. huxlyei* liths (10.5 m^2g) and planktic foraminifera (4.3, Subhas et al., 2018).

Problem Report:
The saturation state of the planktic experiment is anomalously low (0.64). Based on co-located coccolith and calcite dissolution experiments, both the in situ pH and alkalinity appear lower than they should be for that depth. We applied a correction factor of 0.06 to the in situ Omega value to correct for this (i.e. Oca_use = Oca + Oca_corr).

Data Processing Description

BCO-DMO Processing:
Version 1: (2021-08-18)
- Modified column names to comply with BCO-DMO naming conventions;
- Converted dates to ISO8601 format.

Version 2: (2022-08-03)
- Processed new data file received on 2022-08-03;
- Modified column names to comply with BCO-DMO naming conventions;
- Converted dates to ISO8601 format.

Version 2 contains the following updates/corrections:
- In version 1, significant figures appeared cut off in the data. This is corrected in version 2.
- The rate data were pulled from the wrong column from the raw data files and so they were off by a factor of ~2. All of the rates have been updated in version 2.

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Data Files

File
in_situ_dissolution.csv (Comma Separated Values (.csv), 12.41 KB) MD5:452bab63dbce5d737c2024fea40aacd4 Primary data file for dataset ID 856409

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Related Publications

Dong, S., Berelson, W. M., Rollins, N. E., Subhas, A. V., Naviaux, J. D., Celestian, A. J., Liu, X., Turaga, N., Kemnitz, N. J., Byrne, R. H., & Adkins, J. F. (2019). Aragonite dissolution kinetics and calcite/aragonite ratios in sinking and suspended particles in the North Pacific. Earth and Planetary Science Letters, 515, 1–12. https://doi.org/10.1016/j.epsl.2019.03.016
Methods

Naviaux, J. D., Subhas, A. V., Dong, S., Rollins, N. E., Liu, X., Byrne, R. H., … Adkins, J. F. (2019). Calcite dissolution rates in seawater: Lab vs. in-situ measurements and inhibition by organic matter. Marine Chemistry, 215, 103684. doi:10.1016/j.marchem.2019.103684
Methods

Subhas, A. V., Rollins, N. E., Berelson, W. M., Erez, J., Ziveri, P., Langer, G., & Adkins, J. F. (2018). The dissolution behavior of biogenic calcites in seawater and a possible role for magnesium and organic carbon. Marine Chemistry, 205, 100–112. doi:10.1016/j.marchem.2018.08.001
Methods

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Parameters

Parameter	Description	Units
Station	Station number occupied (1-5)	unitless
Lat	Station latitude	degrees North
Long	Station longitude	degrees East
Cast_ID	Cast type: FA = Floating array; HW = hydrowire	unitless
In_ISO_DateTime_UTC	Date and time (UTC) array deployed in ISO 8601 format: YYYY-MM-DDThh:mmZ	unitless
Out_ISO_DateTime_UTC	Date and time (UTC) array recovered in ISO 8601 format: YYYY-MM-DDThh:mmZ	unitless
sample_id	sample type: benthic = benthic foraminifera Amphistegina spp.; ehuxleyi = newly cultured 13C-cultured E. huxleyi; ehuxlyei_orig = original batch of 13C-cultured E. huxleyi; planktic_assemblage = planktic foraminifera assemblage; calcite = 13C-labeled sigma Aldrich inorganic calcite; aragonite = gel-grown 13C-labeled aragonite	unitless
Niskin	Niskin bottle number	unitless
TALK	Total alkalinity	microequivalents per kilogram seawater
pH	pH total scale at zero pressure, 25C, and in situ salinity	unitless
DIC	Calculated DIC	micromoles per kilogram seawater
Depth	Niskin depth	meters (m)
Temp	In situ temperature	degrees Celsius
Salinity	Salinity	unitless
Oca	Calcite saturation state calculated via pH and total alkalinity	unitless
Oar	Aragonite saturation state calculated via pH and total alkalinity	unitless
Rate_ggd	Dissolution rate normalized by carbonate mass	grams per gram per day

Rate_gcm2d	Dissolution rate normalized by carbonate mass and surface area	grams per square centimeter per day
Rate_error_ggd	Dissolution rate error for Rate_ggd	grams per gram per day
Rate_error_gcm2d	Dissolution rate error for Rate_gcm2d	grams per square centimeter per day
log_rate_gcm2d	Log dissolution rate	grams per square centimeter per day
log_rate_error_gcm2d	Log dissolution rate	grams per square centimeter per day
Oca_corr	Omega correction factor, zero except for one planktic foram assemblate experiment.	unitless
Rs	13C ratio of the dissolving solid. Inf = infinity, meaning that there is no 12C (100% 13C-labeled)	moles 13C per mole 12C

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Instruments

Dataset-specific Instrument Name	Modified Niskin incubators
Generic Instrument Name	In-situ incubator
Dataset-specific Description	A 1.6-L Niskin incubator was modified by connecting a PVC sample holder and a Seabird pump to the Niskin via threaded connections and Tygon tubing. The sample holder accommodated packets of 13C-labeled calcium carbonate, and the pump moved seawater from the Niskin interior through the sample holder and back into the Niskin interior. The Seabird pump was run using a custom-built aluminum battery housing strapped to the modified Niskin. See Naviaux et al., (2019) for details.
Generic Instrument Description	A device on a ship or in the laboratory that holds water samples under controlled conditions of temperature and possibly illumination.

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Deployments

KM1712

Website	https://www.bco-dmo.org/deployment/837321
Platform	R/V Kilo Moana
Start Date	2017-08-01
End Date	2017-09-01
Description	Additional cruise information is available from the Rolling Deck to Repository (R2R): https://www.rvdata.us/search/cruise/KM1712

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Project Information

Ocean Acidification - Collaborative Research: Measuring the kinetics of CaCO3 dissolution in seawater using novel isotope labeling, laboratory experiments, and in situ experiments (CaCO3 dissolution)

Coverage: North Pacific, 150 W, 20 to 60 N, all depths

NSF Award Abstract:
Ocean acidification by anthropogenic carbon dioxide (CO2) emissions to the atmosphere will ultimately be balanced by sedimentary carbonate dissolution. The time constant for this reaction, however, is ca. 6,000 years. So, in the coming decades, the ocean's response to CO2 uptake will be based on the kinetics of supply and removal, not on the thermodynamics of the system. Unfortunately our understanding of the basic rate law for carbonate dissolution in the ocean is lacking. The order of the rate law is still argued to be anywhere from 1 to 4.5; this range represents a major difference in the sensitivity of the system to small changes in saturation state. The relative importance of aragonite vs. calcite dissolution, the influence of magnesium content in the minerals, and the sign of the role of organic matter are all still unknowns in the modern ocean. Of course, a truly useful rate law would be able to combine the relative importance of all of these factors into a predictive rule for how dissolution will respond to ocean acidification.

In this study, researchers at the California Institute of Technology and the University of Southern California will address this problem with a novel set of laboratory and in situ experiments that use carbon-13 (13C) tracer labeled biogenic carbonates to measure the dissolution rate under a wide range of saturation states. They will assemble a set of rules that will govern carbonate dissolution in sinking particles and in marine sediments. This will require two sub-projects. First, they will culture several different species of biogenic carbonate producers in the lab under the influence of a strong 13C label. With enrichments of around 30,000o/oo in the calcium carbonate (CaCO3), they will measure the change in dissolved inorganic carbon-13 at several time points over 1-2 weeks in specially built high-pressure reaction chambers. The construction of a prototype chamber is completed and it provides the means, for the first time, to control carbonate saturation state by changing seawater chemistry, pressure, and temperature independently. Experiments with pure 13C labeled inorganic CaCO3 will provide the inorganic reference frame for the biogenic carbonate results. Secondly, to check the lab-based rate data, they will also use labeled biogenic particles in a simple Niskin bottle based reactor that will be deployable on regular hydrowire. The accumulation of 13C in the Niskin dissolved inorganic carbon over 1-2 days will provide an initial rate that is directly comparable to the more extensive laboratory study on the same sorts of materials. Using the San Pedro Basin as a test bed for these in situ experiments will sample a range of saturation states in a series of 3-day cruises. This high-sensitivity approach should allow the team to unpack the various components of carbonate dissolution in seawater under rising CO2 concentrations.

Broader Impacts. Producing a better rate law for carbonate dissolution will have broad implications for the fields of marine chemistry, marine biology, paleoceanography, and for potential societal response to ocean acidification. This rate law sits at the heart of the marine carbonate cycle. In addition, this work will benefit at least two graduate students and promote US-Israel collaborations via the inclusion of Jonathan Erez and his students. The specific involvement of underrepresented high school students in scientific/oceanographic research is built into the efforts of this project as well as ongoing efforts by both PIs to communicate their science to a broad array of non-scientific audiences.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1220600
NSF Division of Ocean Sciences (NSF OCE)	OCE-1220302

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